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U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

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U.S. APPLICATION NO. (If known, see 37 CFR 1.5)

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INTERNATIONAL APPLICATION NO.

PCT/AU00/00393

INTERNATIONAL FILING DATE

28 April 2000

PRIORITY DATE CLAIMED

28 April 1999

TITLE OF INVENTION **COVER GASES**

APPLICANT(S) FOR DO/EO/US

**Nigel Jeffrie RICKETTS et al**

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☐ This is an express request to promptly begin national examination procedures (35 U.S.C. 371(f)).
4. ☐ The US has been elected by the expiration of 19 months from the priority date (PCT Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
  - a. ☐ is attached hereto (required only if not communicated by the International Bureau).
  - b. ☒ has been communicated by the International Bureau.
  - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☐ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
7. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
  - a. ☐ are attached hereto (required only if not communicated by the International Bureau).
  - b. ☐ have been communicated by the International Bureau.
  - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
  - d. ☐ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ An English language translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

**Items 11 to 16 below concern document(s) or information included:**

11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A **FIRST** preliminary amendment.  
☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
14. ☐ A substitute specification.
15. ☐ A change of power of attorney and/or address letter.
16. ☒ Other items or information:

a) **Notification of Transmittal of International Search Report dated 16 June 2000.**b) **PCT International Publication WO 00/64614 dated 2 November 2000,  
with International Search Report dated 16 June 2000.**c) **PCT International Preliminary Examination Report dated 5 September 2001.**

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590-14.pdf

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

Applicants: Nigel Jeffrie RICKETTS et al

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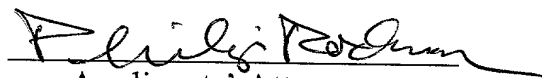
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**PRELIMINARY AMENDMENT  
UNDER MPEP 506 TO REDUCE FILING FEES**

Sir:

Please enter the following amendments before calculating the filing fee for this application:

Please cancel claim 13.

Claim 3, change the claim dependency from "claim 1 or claim 2",  
to --claim 1--.

Claim 4, change the claim dependency from "any one of the preceding claims",  
to --claim 1--.

Claim 5, change the claim dependency from "any one of the preceding claims",  
to --claim 1--.

Claim 6, change the claim dependency from "any one of the preceding claims",  
to --claim 1--.

Claim 7, change the claim dependency from "any one of the preceding claims",  
to --claim 1--.

Claim 8, change the claim dependency from "any one of the preceding claims",  
to --claim 4--.

Claim 9, change the claim dependency from "any one of the preceding claims",  
to --claim 7--.

Claim 10, change the claim dependency from "any one of the preceding claims",  
to --claim 1--.

Claim 14, change the claim dependency from "any one of the preceding claims",  
to --claim 1--.

Claim 15, change the claim dependency from "defined in any one of claims 1-12",  
to --claim 7--.

Claim 16, change the claim dependency from "any one of claims 1-12",  
to --claim 7--.

MARKED-UP VERSION OF AMENDED CLAIMS

3. A composition as claimed in claim 1 [or claim 2] wherein the carrier gas is selected from the group consisting of air, carbon dioxide, argon, nitrogen and mixtures thereof.
4. A composition as claimed in claim 1 [any one of the preceding claims] wherein each component of the composition has GWP of less than 3000.
5. A composition as claimed in claim 1 [any one of the preceding claims] wherein the inhibiting agent is selected from the group consisting of hydrofluorocarbons, hydrofluoroethers and mixtures thereof.
6. A composition as claimed in claim 1 [any one of the preceding claims] wherein the inhibiting agent has a boiling point of less than 100°C.
7. A composition as claimed in claim 1 [any one of the preceding claims] wherein the inhibiting agent is selected from the group consisting of difluoromethane, pentafluoroethane, 1, 1, 1, 2-tetrafluoroethane, difluoroethane, heptafluoropropane, methoxy-nonafluorobutane, ethoxy-nonafluorobutane, dihydrodecafluoropentane and mixtures thereof.
8. A composition as claim in claim 4 [any one of the preceding claims] wherein each component of the composition has a GWP of less than 1500.

9. A composition as claimed in claim 7 [any one of the preceding claims] wherein the inhibiting agent is 1, 1, 1, 2-tetrafluoroethane and the carrier gas is dry air.

10. A composition as claimed in claim 1 [any one of the preceding claims] containing less than 1% by volume inhibiting agent.

14. A method of protecting molten magnesium/magnesium alloy, the method including blanketing the magnesium/magnesium alloy with a cover gas composition as claimed in claim 1 [any one of the preceding claims].

15. Use of an inhibiting agent as claimed in claim 7 [defined in any one of claims 1-12] for preventing or minimizing oxidation of molten magnesium/magnesium alloy.

16. A method of extinguishing a magnesium/magnesium alloy fire, the method including exposing the fire to an atmosphere of an inhibiting agent as defined in claim 7 [any one of claims 1-12].

CLEAN VERSION OF ALL PENDING CLAIMS

1. A cover gas composition for protecting molten magnesium/magnesium alloy, the composition including a fluorine containing inhibiting agent and a carrier gas, wherein each component of the composition has a Global Warming Potential (GWP) (referenced to the absolute GWP for carbon dioxide at a time horizon of 100 years) of less than 5000.
2. A composition as claimed in claim 1 wherein the inhibiting agent has no ozone depletion potential.
3. A composition as claimed in claim 1 wherein the carrier gas is selected from the group consisting of air, carbon dioxide, argon, nitrogen and mixtures thereof.
4. A composition as claimed in claim 1, wherein each component of the composition has GWP of less than 3000.
5. A composition as claimed in claim 1 wherein the inhibiting agent is selected from the group consisting of hydrofluorocarbons, hydrofluoroethers and mixtures thereof.
6. A composition as claimed in claim 1 wherein the inhibiting agent has a boiling point of less than 100°C.

7. A composition as claimed in claim 1 wherein the inhibiting agent is selected from the group consisting of difluoromethane, pentafluoroethane, 1, 1, 1, 2-tetrafluoroethane, difluoroethane, heptafluoropropane, methoxy-nonafluorobutane, ethoxy-nonafluorobutane, dihydrodecafluoropentane and mixtures thereof.

8. A composition as claim in claim 4 wherein each component of the composition has a GWP of less than 1500.

9. A composition as claimed in claim 7 wherein the inhibiting agent is 1, 1, 1, 2-tetrafluoroethane and the carrier gas is dry air.

10. A composition as claimed in claim 1 containing less than 1% by volume inhibiting agent.

11. A composition as claimed in claim 10 containing less than 0.5% by volume inhibiting agent.

12. A composition as claimed in claim 11 containing less than 0.1% by volume inhibiting agent.

14. A method of protecting molten magnesium/magnesium alloy, the method including blanketing the magnesium/magnesium alloy with a cover gas composition as claimed in claim 1.



15. Use of an inhibiting agent as claimed in claim 7 for preventing or minimizing oxidation of molten magnesium/magnesium alloy.

16. A method of extinguishing a magnesium/magnesium alloy fire, the method including exposing the fire to an atmosphere of an inhibiting agent as defined in claim 7.

REMARKS

The foregoing amendments are made for the sole purpose of reducing the filing fee of this application by eliminating the multiple claim dependencies and eliminating the non-statutory claim 13.

Dated: October 26, 2001

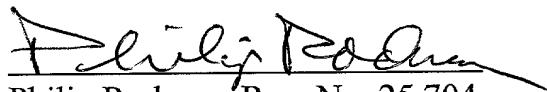
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Respectfully submitted,



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COVER GASESFIELD OF THE INVENTION

5 The present invention relates to compositions useful as cover gases for protecting molten magnesium/magnesium alloys. The present invention also relates to a method for protecting molten magnesium/magnesium alloys and to a method for extinguishing magnesium/magnesium alloy fires.

10 BACKGROUND ART

203050-5 F3F001  
15 Magnesium is a highly reactive and thermodynamically unstable element. Molten magnesium is readily and violently oxidised in ambient air, burning with a flame temperature of approximately 2820°C. Three approaches have been used to inhibit the severe oxidation process. Salt cover fluxes may be sprinkled over the molten metal; oxygen may be excluded from contacting the molten metal by blanketing the molten metal with an inert gas such as helium, nitrogen or argon; or a protective cover gas composition may be used to blanket  
20 the molten metal. Protective cover gas compositions typically comprise air and/or carbon dioxide and a small amount of an inhibiting agent which reacts/interacts with the molten metal to form a film/layer on the molten metal surface which protects it from oxidation. To this day, the  
25 mechanism by which inhibiting agents protect molten reactive metals is not well understood.

US patent no. 1,972,317 relates to methods for inhibiting the oxidation of readily oxidisable metals, including magnesium and its alloys. The patent notes that  
30 at the time of its filing in 1932, numerous solutions had been proposed to the oxidation problem including displacing the atmosphere in contact with the metal with a gas such as nitrogen, carbon dioxide or sulphur dioxide. US 1,972,317 teaches inhibition of oxidation by maintaining in the  
35 atmosphere in contact with molten metal an inhibiting gas containing fluorine, either in elemental or combined form. Reference is made to many fluorine containing compounds with

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the solids ammonium borofluoride, ammonium silicofluoride, ammonium bi-fluoride and ammonium fluophosphate or the gases evolved therefrom upon heating being said to be preferred. Notwithstanding the issue of US 1,972,317 in 1934, it was not until about the mid-1970's that a fluorine containing compound found commercial acceptance as an inhibiting agent in a cover gas.

Prior to about the mid-1970's, sulphur dioxide ( $\text{SO}_2$ ) was widely used as an inhibiting agent in a magnesium cover gas composition but was replaced by sulphurhexafluoride ( $\text{SF}_6$ ) which has become the industry standard. Typically,  $\text{SF}_6$  based cover gas compositions contain 0.2-1% by volume  $\text{SF}_6$  and a carrier gas such as air, carbon dioxide, argon or nitrogen.  $\text{SF}_6$  has the advantages that it is a colourless, odourless, non-toxic gas which can be used for protecting molten magnesium/magnesium alloy and in the production of bright and shiny ingots with relatively low dross formation. However,  $\text{SF}_6$  suffers from several disadvantages. Its sulphur based decomposition products at high temperature are very toxic. It is expensive, has limited sources of supply, and is one of the worst known greenhouse gases having a Global Warming Potential (GWP) at a time horizon of 100 years of 23,900 relative to 1 for carbon dioxide.

It is also noted that once magnesium has ignited, the resulting fire cannot be extinguished even with high concentrations of  $\text{SF}_6$ .  $\text{SO}_2$  is even worse in this respect as it can accelerate a magnesium fire. The only known cover gas for extinguishing a magnesium fire is boron trifluoride ( $\text{BF}_3$ ) which is very expensive and very toxic.

Alternative cover gas compositions are desirable.

#### SUMMARY OF THE INVENTION

In a first aspect, the present invention provides a cover gas composition for protecting molten magnesium/magnesium alloy, the composition including a fluorine containing inhibiting agent and a carrier gas, wherein each component of the composition has a Global Warming Potential (GWP) (referenced to the absolute GWP for

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carbon dioxide at a time horizon of 100 years) of less than 5000.

Preferably, the inhibiting agent has minimal ozone depletion potential, more preferably the inhibiting agent has no ozone depletion potential.

Preferably, the inhibiting agent is non-toxic. In this regard, compounds having a Threshold Limit Value - Time Weighted Average (TLV-TWA) (the time weighted average concentration for a normal 8 hour workday and a 40 hour workweek, to which nearly all workers may be repeatedly exposed, day after day, without adverse effect) as issued by the American Conference of Governmental Industrial Hygienists of less than 100ppm are considered to be toxic. By way of example,  $\text{BF}_3$ , silicon tetrafluoride ( $\text{SiF}_4$ ), nitrogen trifluoride ( $\text{NF}_3$ ) and sulfuryl fluoride ( $\text{SO}_2\text{F}_2$ ) disclosed in US 1972317 are toxic.

The composition may include a mixture of inhibiting agents (each having a GWP less than 5000) and preferably comprises a minor amount of inhibiting agent and a major amount of a carrier gas. Preferably, the composition consists of less than 1% by volume inhibiting agent and the balance carrier gas. More preferably, the composition contains less than 0.5% by volume (most preferably less than 0.1% by volume) inhibiting agent.

Preferably, each component of the composition has a GWP of less than 3000, more preferably, less than 1500.

Suitable carrier gases include air, carbon dioxide, argon, nitrogen and mixtures thereof.

The inhibiting agent may be selected from the group consisting of hydrofluorocarbons (HFCs), hydrofluoroethers (HFEs) and mixtures thereof. Preferably, the inhibiting agent has a boiling point of less than  $100^\circ\text{C}$ , more preferably less than  $80^\circ\text{C}$ . Where the inhibiting agent is gaseous at ambient temperature, it may be diffused in the carrier gas at the desired concentration. Where the inhibiting agent is liquid at ambient temperature, it may be entrained in the carrier gas to a desired concentration by

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passing a flow of carrier gas over the inhibiting agent. Suitable hydrofluorocarbons and hydrofluoroethers are listed in Table 1 below which includes their boiling points (BP) and their GWP's (referenced to the absolute GWP for carbon dioxide at a time horizon of 100 years) which have been sourced from IPCC 1996.

2000-01-01

TABLE 1

Chemical Name	Industry Name	Formula	GWP	BP
difluoromethane	HFC-32	$\text{CH}_2\text{F}_2$	580	-52°C
pentafluoroethane	HFC-125	$\text{C}_2\text{HF}_5$	3,200	-49°C
1,1,1,2-tetrafluoroethane	HFC-134a, R134a	$\text{C}_2\text{H}_2\text{F}_4$	1,300	-26°C
difluoroethane	HFC-152a, R152a	$\text{C}_2\text{H}_4\text{F}_2$	140	-27°C
heptafluoropropane	HFC-227ea	$\text{C}_3\text{HF}_7$	2,900	-17°C
methoxy-nonafluorobutane	HFE-7100	$\text{C}_4\text{F}_9\text{OCH}_3$	480	61°C
ethoxy-nonafluorobutane	HFE-7200	$\text{C}_4\text{F}_9\text{OC}_2\text{H}_5$	90	78°C
dihydrodecafluoropentane	HFC-43-10-mee	$\text{C}_5\text{H}_2\text{F}_{10}$	1,300	54°C

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A preferred cover gas composition consists of 1,1,1,2-tetrafluoroethane and dry air. Experimental work has demonstrated that such a cover gas composition provides protection at least the equal of SF<sub>6</sub> based compositions and can be utilised at lower concentrations of inhibiting agent. SF<sub>6</sub> has a GWP in excess of 18 times that of 1,1,1,2-tetrafluoroethane and is presently more than 2½ times the cost of 1,1,1,2-tetrafluoroethane.

In a second aspect, the present invention provides a method of protecting molten magnesium/magnesium alloy, the method including blanketing the molten magnesium/magnesium alloy with a cover gas composition according to the first aspect of the present invention.

The method according to the second aspect of the present invention is applicable to protecting molten magnesium/magnesium alloy in a foundry vessel such as a furnace and during casting.

In a third aspect, the present invention provides use of an inhibiting agent as defined with respect to the first aspect of the present invention for preventing or minimising oxidation of molten magnesium/magnesium alloy. By way of example, an inhibiting agent of the present invention may be used to prevent or minimise oxidation of molten magnesium/magnesium alloy during sand casting. Where the inhibiting agent is gaseous at ambient temperature, the sand mould may be purged with inhibiting agent prior to pouring of the molten metal. Where the inhibiting agent is liquid at ambient temperature, the sand mould may be sprayed with inhibiting agent from a squeeze bottle or the like prior to pouring of the molten metal. Other suitable methods of using inhibiting agents of the present invention to prevent or minimise oxidation of molten magnesium/magnesium alloy will be readily apparent to those of skill in the art of foundry practice.

In a fourth aspect, the present invention provides a method of extinguishing a magnesium/magnesium alloy fire, the method including exposing the fire to an atmosphere of

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an inhibiting agent as defined with respect to the first aspect of the present invention. The fire may be so exposed by, for example, subjecting it to a flow of the inhibiting agent or immersing it in a reservoir containing the inhibiting agent.

#### EXAMPLES

The ensuing non-comparative Examples are illustrative of preferred embodiments of the present invention and are not to be construed as limiting the scope of the present invention in any way.

##### **Example 1**

A crucible furnace containing 100 grams of molten pure magnesium at 680°C was blanketed with a gaseous composition consisting of 0.02% by volume 1,1,1,2-tetrafluoroethane and the balance dry air. Good molten magnesium protection was observed, with the formation of a thin protective surface film. Deliberate rupturing of the surface film did not induce burning of the molten magnesium sample.

##### **Comparative Example 1**

Comparative Example 1 was identical to Example 1 with the exception that 1,1,1,2-tetrafluoroethane was replaced by SF<sub>6</sub>. Good molten magnesium protection was not observed, and the magnesium sample burned rapidly. Adequate protection of the molten magnesium sample was only achieved when the gaseous composition consisted of 0.05% by volume SF<sub>6</sub> and the balance dry air. At this concentration of SF<sub>6</sub>, deliberate rupturing of the surface film resulted in localised burning of the molten magnesium sample.

Example 1 and Comparative Example 1 demonstrate that the inventive cover gas composition provides good protection of molten magnesium at a lower concentration than an SF<sub>6</sub> based composition.



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**Example 2**

A series of single ingots of both pure magnesium and magnesium-aluminium alloy AZ91 were cast in an 8kg ingot mould within a controllable atmosphere chamber. The molten metal was sucked under vacuum into the chamber to fill the ingot mould. When the ingot mould was full, the vacuum was turned off, the chamber was filled with a cover gas composition, and the molten metal was allowed to solidify. In the case of AZ91 alloy the cover gas composition consisted of 0.04% by volume 1,1,1,2-tetrafluoroethane and the balance dry air. The cover gas composition for the pure magnesium casting consisted of 0.1% by volume 1,1,1,2-tetrafluoroethane and the balance dry air.

Single ingots of both pure magnesium and AZ91 alloy were produced free of burning, with bright shiny surface finishes, with very low levels of dross, and with no reaction with boron nitride mould coatings.

**Comparative Example 2**

Comparative Example 2 was identical to Example 2 with the exception that 1,1,1,2-tetrafluoroethane was replaced by SF<sub>6</sub> which was used at the same concentrations, ie. 0.04% by volume in dry air for AZ91 alloy and 0.1% by volume in dry air for pure magnesium.

The ingots produced in Example 2 had lower levels of dross and had a more attractive surface finish than those produced in Comparative Example 2.

**Example 3**

A small flow of 1,1,1,2-tetrafluoroethane was continuously metered into a container that is used to collect molten magnesium dross. During transport of the dross from the furnace to the container, the dross contacted the air and ignited. Upon placing the dross into the container, the burning quickly stopped.

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**Comparative Example 3**

Comparative Example 3 was identical to Example 3 with the exception that 1,1,1,2-tetrafluoroethane was replaced by  $\text{SF}_6$ . In this case, the dross continued to burn after being  
5 placed into the container.

Example 3 and Comparative Example 3 demonstrate that an inhibiting agent of the present invention is able to suppress the burning of magnesium metal/dross. This enables minimisation of magnesium fume in a working environment and  
10 prevention of oxidation of the magnesium metal content in the dross. This would enable dross processing operations to recover valuable magnesium metal content.

**Example 4**

15 Ingots of pure magnesium were cast in 8kg ingot moulds on an industrial-sized ingot casting machine having a controllable atmosphere chamber. The casting machine was operated at a casting rate of 3 tonnes of cast metal per hour with 330 litres per minute dry air and 3.3 litres per  
20 minute 1,1,1,2-tetrafluoroethane introduced into the chamber. Ingots were produced free of burning, with bright shiny surface finishes, with very low levels of dross and with no reaction with boron nitride mould coatings.

**Comparative Example 4**

25 Comparative Example 4 was identical to Example 4 with the exception that 1,1,1,2-tetrafluoroethane was replaced by  $\text{SF}_6$ , which was used at the same flow rate and at the same concentration in dry air. Ingots produced in Comparative  
30 Example 4 exhibited similar properties to those produced in Example 4.

Example 4 and Comparative Example 4 demonstrate that the inventive gas can successfully replace  $\text{SF}_6$  for industrial scale continuous production of magnesium ingot.

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**Example 5**

A series of single ingots of pure magnesium were cast in an 8kg ingot mould within a controllable atmosphere chamber. The molten metal was sucked under vacuum into the chamber to fill the ingot mould. When the ingot mould was full, the vacuum was turned off, the chamber was filled with cover gas composition, and the molten metal was allowed to solidify. The cover gas composition was produced by passing 0.5 litres per minute of dry air over 50ml of the HFE liquid methoxy-nonafluorobutane. The resulting gas phase mixture flowed to the single ingot casting apparatus. Single ingots were produced free of burning, with bright shiny surface finishes, with very low levels of dross and with no reaction with boron nitride mould coatings.

**Example 6**

A series of single ingots of pure magnesium were cast in an 8kg ingot mould within a controllable atmosphere chamber. The molten metal was sucked under vacuum into the chamber to fill the ingot mould. When the ingot mould was full, the vacuum was turned off, the chamber was filled with a cover gas composition, and the molten metal was allowed to solidify. The cover gas composition was produced by passing 0.5 litres per minute of dry air over 50ml of the HFC liquid dihydrodecafluoropentane. The resulting gas phase mixture flowed to the single ingot casting apparatus. Single ingots were produced free of burning, with bright shiny surface finishes, with very low levels of dross and with no reaction with boron nitride mould coatings.

**Example 7**

A furnace containing 20kg of molten magnesium at 700°C was blanketed with a cover gas composition. The cover gas composition was produced by passing 0.6 litres per minute of dry air over 50ml of the HFE liquid methoxy-nonafluorobutane. The resulting gas phase mixture flowed to the furnace. Good molten magnesium protection was observed,

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with the formation of a thin protective surface film. Deliberate rupturing of the surface film did not induce burning of the molten magnesium sample.

5 **Example 8**

10 A furnace containing 20kg of molten magnesium at 700°C was blanketed with a cover gas composition. The cover gas composition was produced by passing 0.9 litres per minute of dry air over 50ml of the HFE liquid ethoxy-nonafluorobutane. The resulting gas phase mixture flowed to the furnace. Good molten magnesium protection was observed, with the formation of a thin protective surface film. Deliberate rupturing of the surface film did not induce burning of the molten magnesium sample.

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**Example 9**

20 A furnace containing 20kg of molten magnesium at 700°C was blanketed with a cover gas composition. The cover gas composition was produced by passing 0.9 litres per minute of dry air over 50ml of the HFC liquid dihydrodecafluoropentane. The resulting gas phase mixture flowed to the furnace. Good molten magnesium protection was observed, with the formation of a thin protective surface film. Deliberate rupturing of the surface film did not induce burning of the molten magnesium sample.

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**Example 10**

30 A furnace containing 20kg of molten magnesium at 700°C was blanketed with a gaseous composition consisting of 0.4% by volume difluoroethane and the balance dry air. Good molten magnesium protection was observed, with the formation of a thin protective surface film. Deliberate rupturing of the surface film did not induce burning of the molten magnesium sample.

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**Comparative Example 10**

Comparative Example 10 was identical to Example 10 with the exception that difluoroethane was replaced by  $\text{SF}_6$ , which was used at the same concentration. Good molten magnesium protection was observed.

Example 10 and Comparative Example 10 demonstrate that an inhibiting agent of the present invention provides equivalent protection of molten magnesium metal compared to  $\text{SF}_6$ .

**Example 11**

Magnesium squeeze-castings were produced by hand-pouring molten magnesium into the shot sleeve of a vertical injection squeeze casting machine. Prior to pouring the molten magnesium into the shot sleeve, a small volume of pure 1,1,1,2-tetrafluoroethane was introduced into the shot sleeve. This protected the molten magnesium in the shot sleeve and prevented the molten magnesium from burning during the filling of the mould.

**Example 12**

Various magnesium components were produced using the investment casting technique. Prior to filling the investment casting shell with molten magnesium, the shell was purged with pure 1,1,1,2-tetrafluoroethane. This prevented the magnesium from burning while solidifying inside the shell. Upon cooling, the shell mould was removed. The magnesium casting exhibited a good surface finish.

**Example 13**

Various magnesium components were produced using the sand casting technique. Prior to filling the sand mould with molten magnesium, the sand mould was purged with pure

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[illegible]

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### Comparative Example 14

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CLAIMS

1. A cover gas composition for protecting molten magnesium/magnesium alloy, the composition including a fluorine containing inhibiting agent and a carrier gas, wherein each component of the composition has a Global Warming Potential (GWP) (referenced to the absolute GWP for carbon dioxide at a time horizon of 100 years) of less than 5000.
2. A composition as claimed in claim 1 wherein the inhibiting agent has no ozone depletion potential.
3. A composition as claimed in claim 1 or claim 2 wherein the carrier gas is selected from the group consisting of air, carbon dioxide, argon, nitrogen and mixtures thereof.
4. A composition as claimed in any one of the preceding claims wherein each component of the composition has a GWP of less than 3000.
5. A composition as claimed in any one of the preceding claims wherein the inhibiting agent is selected from the group consisting of hydrofluorocarbons, hydrofluoroethers and mixtures thereof.
6. A composition as claimed in any one of the preceding claims wherein the inhibiting agent has a boiling point of less than 100°C.
7. A composition as claimed in any one of the preceding claims wherein the inhibiting agent is selected from the group consisting of difluoromethane, pentafluoroethane, 1,1,1,2-tetrafluoroethane, difluoroethane, heptafluoropropane, methoxy-nonafluorobutane, ethoxy-nonafluorobutane.

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dihydrodecafluoropentane and mixtures thereof.

- 5 8. A composition as claimed in any one of the preceding claims wherein each component of the composition has a GWP of less than 1500.
- 10 9. A composition as claimed in any one of the preceding claims wherein the inhibiting agent is 1,1,1,2-tetrafluoroethane and the carrier gas is dry air.
- 10 10. A composition as claimed in any one of the preceding claims containing less than 1% by volume inhibiting agent.
- 15 11. A composition as claimed in claim 10 containing less than 0.5% by volume inhibiting agent.
12. A composition as claimed in claim 11 containing less than 0.1% by volume inhibiting agent.
- 20 13. A cover gas composition substantially as herein described in any non-comparative Example.
- 25 14. A method of protecting molten magnesium/magnesium alloy, the method including blanketing the magnesium/magnesium alloy with a cover gas composition as claimed in any one of the preceding claims.
- 30 15. Use of an inhibiting agent as defined in any one of claims 1-12 for preventing or minimising oxidation of molten magnesium/magnesium alloy.
- 35 16. A method of extinguishing a magnesium/magnesium alloy fire, the method including exposing the fire to an atmosphere of an inhibiting agent as defined in any one of claims 1-12.



**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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Published

With international search report.

(54) Title: COVER GASES

(57) Abstract

A cover gas composition for protecting molten magnesium/magnesium alloy includes a fluorine containing inhibiting agent and a carrier gas. Each component of the composition has a Global Warming Potential (GWP) (referenced to the absolute GWP for carbon dioxide at a time horizon of 100 years) of less than 5000.

**DECLARATION FOR PATENT APPLICATION**

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name,

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

COVER GASES

the specification of which is attached hereto unless the following box is checked:

☒ was filed on \_\_\_\_\_ as United States Application Number \_\_\_\_\_  
or PCT International Application Number PCT/AU00/00393  
and was amended on \_\_\_\_\_  
(if applicable)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR §1.56.

I hereby claim foreign priority benefits under 35 U.S.C. §119(a)-(d) or §365(b), of any foreign application(s) for patent or inventor's certificate, or §365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, any foreign application for patent or inventor's certificate, or PCT International application, having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s)			Priority Claimed	
<u>PCT/AU00/00393</u>	<u>International</u>	<u>28 April 2000</u>	<input checked="" type="checkbox"/>	<input type="checkbox"/>
(Number)	(Country)	(Day/Month/Year Filed)	Yes	No
<u>PQ0015</u>	<u>Australia</u>	<u>28 April 1999</u>	<input checked="" type="checkbox"/>	<input type="checkbox"/>
(Number)	(Country)	(Day/Month/Year Filed)	Yes	No

I hereby claim the benefit under 35 U.S.C. §119(e) of any United States provisional application(s) listed below.

\_\_\_\_\_  
(Application Number)

\_\_\_\_\_  
(Filing Date)

\_\_\_\_\_  
(Application Number)

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(Filing Date)

\_\_\_\_\_  
(Application Number)

\_\_\_\_\_  
(Filing Date)

I hereby claim the benefit under 35 U.S.C. §120 of any United States application(s), or §365© of any PCT International application designating the United States listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application or PCT International application in the manner provided by the first paragraph of 35 U.S.C. §112, I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR §1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application:

PCT/AU00/00393      28 April 2000      Pending  
(Application Serial No.)      (Filing Date)      (Status – patented, pending, abandoned)

(Application Serial No.)      (Filing Date)      (Status – patented, pending, abandoned)

I (we) hereby appoint the following as our representative(s) to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith:

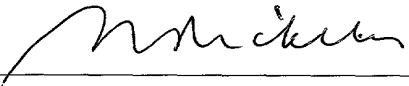
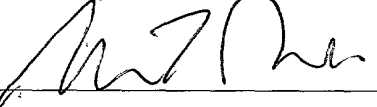
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I (we) hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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